PATENT SPECIFICATION

(11) 1209 590

1 209 590

NO DRAWINGS

(21) Application No. 22592/69 (22) Filed 2 May 1969
(31) Convention Application No. P 17 71 312.1
(32) Filed 4 May 1968 in
(33) Germany (DT)
(45) Complete Specification published 21 Oct. 1970
(51) International Classification C 03 c 3/08
(52) Index at acceptance
C1M 11B1 11C11 11C12 11C3 11C5 11C7 11C8 11C9 11F1 11F10 11F15 11F2 11F20 11F24 11F3 11F30 11F33 11F4 11F5 11J2 11J3 11K1 11K5 11K9

(54) IMPROVEMENTS IN OR RELATING TO GLASS

(71) We, CARL-ZEISS-STIFTUNG, a Foundation established under the laws of Germany, of Heidenheim a.d. Brenz, Wurttemberg, Germany, trading as JENAer GLASWERK SCHOTT & GEN., do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a fluorine-containing borosilicate glass.

It is known that wave fronts are deformed in a glass when the optical path length is of different value at different parts of the glass because of temperature gradients which occur.

Optical instruments in space vehicles are exposed to strong temperature differences for example, due to temporary exposure to solar radiation and due to subsequent ratiation into space, and also by emitted and/or reflected infra-red rays from close planets. These temperature differences can cause wave deformations in the optical glasses, and such waves considerably reduce the resolving power of the optical systems.

Also in connection with aerial photography, for example, the temperature gradients which are established can considerably reduce the resolution. Accordingly, there is a great demand for optical systems and optical sealing windows consisting of glasses with an optical path length not dependent on temperature.

With planoparallel sealing windows, for example, the change in optical path length resulting from the change in temperature is

$$\Delta W = W_1 - W_2 = d \cdot G . \Delta t = d . \left\{ \alpha (n-1) + \frac{dn}{dt} \right\} . \Delta t$$

A disturbing wave deformation is caused when ΔW is of different value at different places of the sealing window because of temperature gradients which are set up. W is the optical wavelength, t is the temperature and n is the refractive index. The equation shows that the optical path difference ΔW can be decreased by reducing the thickness d of the glass element, the temperature difference Δt or the value $G = (n-1)\alpha + \frac{dn}{dt}$, The expansion coefficient is denoted by α. The value G only depends on the physical properties of the glass and should be as small as possible, being 0 in the ideal case. The value G is a characteristic value defined in terms of refractive index, expansion coefficient and rate of change of refractive index with temperature. The $\frac{dn}{dt}$ value must therefore be negative. This seems possible by the introduction of glass components

1) which cause the best possible increase in the coefficient of thermal expansion,

2a) which so influence the glass that the dependance on temperature of the ultraviolet characteristic frequency $\left[\frac{d\lambda o}{dt}\right]$ remains as small as possible, and/or

2b) which produce a displacement of the ultraviolet characteristic frequencies λ_o of the glass towards small wavelengths.

However, the increase in the thermal expansion which is necessary according to 1) makes it difficult to maintain the condition G=0, since the temperature coefficient $\frac{dn}{dt}$ must assume very high negative values on account of the resultant raising of the term

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$(n-1)$. a. This contrast clearly shows the difficulties which exist when developing glasses with an optical path length not dependant on temperature.

It is thus the object of the present invention to provide a glass with which the disturbing influence of a temperature gradient on the image-forming properties is substantially excluded.

According to this invention we provide a fluorine-containing borosilicate glass consisting of the following constituents expressed as weight percentages:

(i)	SiO_2	14 — 63
(ii)	B_2O_3	6 — 20
(iii)	Al_2O_3	5 — 18
(iv)	Alkali metal oxide(s) and/or alkali metal fluoride(s)	8 — 20.2
(v)	Sb_2O_3	1.5 — 32
(vi)	F other than that contained in (iv)	1 — 12
(vii)	ZnO	0 — 2
(viii)	CdO	0 — 2
(ix)	GeO_2	0 — 10
(x)	WO_3	0 — 3
(xi)	Ta_2O_5	0 — 4
(xii)	Nb_2O_5	0 — 15
(xiii)	Bi_2O_3	0 — 15
(xiv)	SO_4^{--}	0 — 8
(xv)	As_2O_3	0 — 5
(xvi)	PbO	0 — 10
(xvii)	Alkaline earth metal oxide(s)	0 — 1

Item (iv) may be chosen from the following components expressed as weight percentages:

K_2O	0 — 18
Na_2O	0 — 14
Rb_2O	0 — 5
Cs_2O	0 — 5
Li_2O	0 — 5
KF	0 — 18

Preferably item (iv) is K_2O and/or KF. Expediently at least 40% of the glass is represented by items (i), (ii) and (iii).

Fluorine can be supplied as fluoride (e.g. KF, AlF_3), as difluoride (e.g. KHF_2) or in other form (e.g. as silicofluoride) to the melt. The n values of the glasses according to the invention are generally greater than 1.44 and the γ_d values are generally less than 70.

By introducing up to 8% by weight of SO_4^{--} (e.g. as $Al_2(SO_4)_3$), a strong increase in the viscosity is caused and it has additional influence on the main and partial dispersions of the glass.

In glasses having a basis of SiO_2, the glass components fluorine, B_2O_3 and K_2O shift the $\frac{dn}{dt}$-values in a negative direction, without substantially increasing the thermal expansion.

The fluorine component also has the effect that the independance of the ultra-violet characteristic frequency $\frac{d\lambda o}{dt}$ on temperature remains as small as possible. Increasing B_2O_3 content displaces the ultra-violet characteristic frequency λ_o towards short wavelengths, and Sb_2O_3 does not unfavourably change the ultra-violet characteristic frequency λ_o.

Examples of compositions expressed as weight percentages of the glasses embodying this invention are given with their physical properties in the following Table.

	1	2	3	4	5	6	7	8
SiO_2	48.9	49.8	44.5	41.5	37.3	38.1	36.5	37.0
B_2O_3	14.9	17.2	17.8	15.2	15.3	17.7	13.2	9.6
Al_2O_3	6.5	7.1	14.3	15.2	13.7	14.4	12.8	11.5
Li_2O								
Na_2O	0.1	0.3	1.4	0.3	0.3	0.5	0.1	2.0
K_2O	6.2	6.3	3.5	3.3	3.0	3.1	2.9	12.5
Sb_2O_3	9.8	4.7	4.7	4.7	14.6	9.5	19.7	13.8
KF	12.5	13.4	12.6	16.6	13.7	14.6	12.9	
AlF_3	0.8	0.9	0.9	2.9	1.8	1.8	1.6	13.3
WO_3								
Nb_2O_5								
$Al_2(SO_4)_3$								
PbO								
As_2O_3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
F^-	4.3	4.5	4.2	5.6	4.5	4.8	4.3	3.8
SO_4^{--}								
n_d	1.4924	1.4822	1.4710	1.4619	1.4875	1.4718	1.4952	1.4799
d	61.1	64.5	62.2	63.0	55.1	58.9	51.9	55.8
$\alpha.10^{-7}/°C$		95	90	108	100	104	96	
$\frac{\Delta n}{\Delta +}$ abs. * (20—40°C) for + 546.1		−3.3	−4.3	−4.8,	−4.5	−4.6	−4.7	
G abs.+(H—1) $\alpha + \frac{\Delta n}{\Delta t}$	+1.4	+1.3	−0.1	+0.2	+0.4	+0.3	+0.5	

* Change in refractive index with respect to vacuum.

	9	10	11	12	13	14	15	16	17
SiO_2	36.2	34.0	34.8	29.2	38.3	35.4	34.6	25.1	15.8
B_2O_3	7.2	8.7	16.9	11.0	11.0	10.2	10.3	17.4	15.1
Al_2O_3	11.2	9.2	9.8	10.8	12.3	11.4	11.4	14.3	14.3
Li_2O									0.3
Na_2O	12.5	—	3.5	0.1	0.1	0.1	0.1	0.5	0.5
K_2O	—	11.0	10.9	1.2	8.7	8.1	8.1	1.5	1.5
Sb_2O_3	10.0	22.2	9.5	16.5	19.5	25.2	25.3	18.8	30.4
KF		3.1		13.9	7.3	6.9	6.6	15.8	15.8
AlF_3	18.3	11.5	14.3	1.4	1.9	1.8	1.5	6.0	6.0
WO_3					0.1	0.1	0.5		
Na_2O_5							1.1		
$Al_2(SO_4)_3$				15.6					
PbO	4.3				0.5	0.5	0.4		
As_2S_3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
F^-		1.2		4.8	2.5	2.5	2.5	5.5	5.5
SO_4^{--}			6.0						
n_d	1.4978	1.5045	1.4957	1.5068	1.5111	1.5262	1.5334	1.4930	1.5142
d	53.4	49.8	56.0	50.9	50.6	47.0	45.4	51.5	44.7

PRODUCTION EXAMPLE:

A batch consisting of 750 kg. of silicon dioxide, 460 kg. of boron oxide, 145 kg. of aluminium hydroxide, 8 kg. of sodium carbonate, 140 kg. of potassium carbonate, 71 kg. of antimony trioxide, 201 kg. of potassium fluoride, 13.5 kg. of aluminium fluoride and 4.5 kg. of arsenic trioxide is thoroughly mixed in a commercial mixer. After introduction and complete melting of the bath in a ceramic basin at 1380°C., for which about 12 hours are required, the melt is refined for 8 hours at 1400°C. The furnace temperature is thereafter allowed to fall while stirring constantly until the glass has assumed the viscosity of about 400 poises which is suitable for pouring. The glass is then poured into a preheated iron mould and then cooled to room temperature. A glass is obtained which corresponds to Example 2 in the Table. The cooling from the transformation point Tg (360°C.) down to room temperature is a 1°C./hour, i.e. takes about 14 days.

WHAT WE CLAIM IS:—

1. A fluorine-containing borosilicate glass consisting of the following constituents expressed as weight percentage:

(i)	SiO_2	14 — 63
(ii)	B_2O_3	6 — 20
(iii)	Al_2O_3	5 — 18
(iv)	Alkali metal oxide(s) and/or alkali metal fluoride(s)	8 — 20.2
(v)	Sb_2O_3	1.5 — 32
(vi)	F other than that contained in (iv)	1 — 12
(vii)	ZnO	0 — 2
(viii)	CdO	0 — 2
(ix)	GeO_2	0 — 10
(x)	WO_3	0 — 3
(xi)	Ta_2O_5	0 — 4
(xii)	Nb_2O_5	0 — 15
(xiii)	Bi_2O_3	0 — 15
(xiv)	SO_4	0 — 8
(xv)	As_2O_3	0 5
(xvi)	PbO	0 — 10
(xvii)	Alkaline earth metal oxide(s)	0 — 1

2. A glass according to Claim 1, wherein item (iv) is chosen from the following components expressed as weight percentages:

K_2O	0 — 18
Na_2O	0 — 14
Rb_2O	0 — 5
Cs_2O	0 — 5
Li_2O	0 — 5
KF	0 — 18

3. A glass according to Claim 1, wherein item (iv) is K_2O and/or KF.

4. A glass according to any preceding claim, wherein at least 40% by weight of the glass is represented by items (i), (ii) and (iii).

5. A glass substantially as herein described and exemplified.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1970.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

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